Disordering to Order: de Vries behavior from a Landau theory for smectics

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(Dated: February 6, 2008)

We show that Landau theory for the isotropic (I), nematic (N), smectic A, and smectic C phases generically, but not ubiquitously, implies "de Vries" behavior. I.e., a continuous AC transition can occur with little layer contraction; the birefringence decreases as temperature T is lowered above this transition, and increases again below the transition. This de Vries behavior occurs in models with unusually small orientational order, and is preceded by a first order $I-A$ transition. A first order AC transition with elements of de Vries behavior can also occur. These results correspond well with experimental work to date.

Recently, an unusual new class of liquid crystals known as "de Vries smectics" [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] has drawn interest. They possess two defining features [11]. Firstly, there is little change with temperature T of the layer spacing $d(T)$ in the C phase, in contrast to the rapid geometrical contraction $d(T) \propto \cos\theta(T)$ expected if the molecules tilt by a strongly temperature angle $\theta(T)$. Secondly, the A phase birefringence shows a nonmonatonic temperature dependence [12], initially increasing as T is lowered, then decreasing as the AC transition is approached. This is the first example known to us of *decreasing* order as a lower symmetry phase is approached. Generally, de Vries smectics exhibit the phase sequence $I-A-C$, without a nematic phase, and an AC transition that is second order, although in some it is weakly first order [9].

The generally accepted picture of these materials is de Vries' diffuse cone model [13], which says that as the AC transition is approached from the A phase, the molecules "pre-tilt" , but in azimuthally random directions (hence reducing orientational order), so that there is no long range order in the tilting. Upon entering the C phase the molecules azimuthally order without the significant layer contraction that occurs in conventional smectics whose molecules tilt at the AC transition[2, 4, 5, 8, 13, 14, 15].

In this Letter we show that in a complete, nonchiral Landau mean field theory for the isotropic (I), nematic (N), A and C phases, in which all three order parameters (orientational, layering, azimuthal tilt) and the layer spacing are coupled, de Vries behavior occurs in a finite fraction of parameter space (namely, for unusually weak coupling between layering and orientational order), while other regions exhibit conventional behavior. The mean field phase diagram for our model is shown in Fig. 1. Here t_s and t_n are Landau theory parameters that control layering, and orientational order, respectively.

Note that this phase diagram predicts *two*, distinct smectic A phases of identical symmetry, denoted A and A', separated by a first order phase transition. While first order transitions between two smectic A phases due to competition between two different layer spacings[16] have been predicted, our result shows that even without such competition, $A-A$ transitions occur quite naturally, and should be far more common than was previously thought.

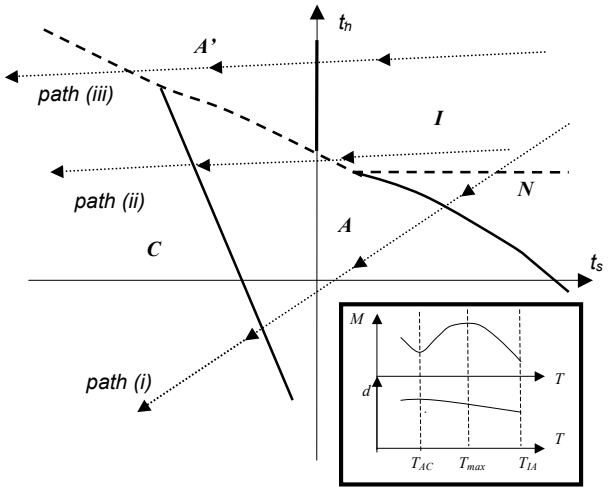

FIG. 1: The phase diagram in t_s-t_n space for the I, N, A, C phases. First and second order phase boundaries are shown as dashed and solid lines respectively.Three decreasing temperature paths from the I to C phase are shown. Path (i) corresponds to a conventional material that does not exhibit de Vries behavior. Path (ii) corresponds to a material exhibiting de Vries behavior and a second order AC transition. Path (iii) leads to a first order AC transition with elements of de Vries behavior. The inset shows the qualitative dependence on temperature of birefringence (M) and layer spacing (d).

Any experiment in which temperature is varied at fixed concentration corresponds to a particular path through this phase diagram. As usual in Landau theory, we assume throughout this paper that t_s and t_n are mono-

tonically increasing functions of temperature; hence, as temperature is lowered, one moves monotonically from upper right to lower left in Fig. 1. Three qualitatively distinct paths of this type are shown. Path (i) is a typical path for a material that does *not* display de Vries behavior; along it, both t_s *and* t_n both depend strongly on temperature. Paths (ii) and (iii) correspond to de Vries behavior with 2nd and 1st order AC and $A'C$ transitions, respectively. Both paths have strongly varying t_s and weakly varying t_n; i.e, t_n is virtually athermal. This would be the case if the IN transition is driven by a steric mechanism for which t_n depends strongly on concentration and weakly on T. We find that de Vries behavior occurs in this case, for sufficiently weak coupling between layering and orientational orders.

This restriction to nearly horizontal paths implies that de Vries systems should very rarely exhibit an N phase between the A and C phases, since, to cross the IN boundary, a nearly horizontal path in Fig. 1 would have to be "fine tuned" to start very close to the boundary. The most likely paths to see de Vries behavior are those like (ii) or (iii), showing phase sequence $I-A-C$ or $I-A'-C$. This phase sequence is in good agreement with experimental work to date.

In this Letter we focus on path (ii) and briefly discuss path (iii) at the end. The inset in Fig. 1 shows our predictions for the layer spacing $d(T)$ and birefringence $M(T)$ as T is varied along path (ii). The *increase* of the layer spacing in the A phase as the AC transition is approached, though contrary to the de Vries picture of "pre-tilting" in the A phase, is seen experimentally [3].

In the A-phase, our Landau theory predicts:

$$M_A(T) \;=\; M_{max} - M_2\left[\frac{t_s(T)-t_s(T_{max})}{t_s(T_{max})}\right]^2, \quad (1)$$

where M_{max} , M_2 and T_{max} are positive constants. For a finite range of Landau parameters, on path (ii) $T_{IA} < T_{max} < T_{AC}$, where T_{IA} and T_{AC} are the IA and AC transition temperatures, respectively, and M has a maximum *within* the A phase. Hence, $M(T)$ is nonmonatonic (the second defining feature of de Vries behavior). If t_s is linear in T in the A-phase (as expected for small $T_{IA}-T_{AC}$), then $M(T)$ will be *perfectly* parabolic in T.

Near the AC transition within the C phase the critical temperature dependences of M and the tilt angle $\theta(T)$ predicted by our Landau theory are: M linear in T, and $\theta \propto (T_{AC}-T)^{\frac{1}{2}}$. When fluctuation effects are included, we expect[18] $\theta \propto (T_{AC}-T)^{\beta}$, where $\beta \approx 0.35$ is the order parameter critical exponent for the 3D XY model. The layer spacing scales with temperature according to:

$$d = d_0 + a(T_{AC}-T) + b(T_{AC}-T)^3\,, \quad (2)$$

where d_0 is the value of the layer spacing *at* the AC transition and a and b are constants that depend on the Landau theory parameters . Clearly, if a is sufficiently small, which we find is the case in the C phase for sufficiently weak coupling between layering and orientational order, the layer spacing shows very little variation with temperature near T_{AC}. Significantly, we find that in cases like path (ii), the criterion for de Vries behavior of $d(T)$ differs from that for $M(T)$. Hence, we predict that some systems will exhibit de Vries behavior of the layer spacing, but *not* of the birefringence, and others the reverse.

While Landau theory predicts that the $I-A'$ transition is continuous, it is known[17] that fluctuations *always* drive the $I-A'$ transition first order, albeit only *weakly* so if fluctuations are small. Fluctuation effects will also shift the the positions of *all* of the transitions we've found. We expect, however, that the topology and essential geometry of the phase diagram Fig. 1 should occur in real systems. The only qualitative difference we expect is that the $I-A-A'$ critical end point (CEP) predicted by Landau theory will be replaced by an $I-A-A'$ *triple* point. In other regions of parameter space, our model has an NAC point; we will discuss this elsewhere[19].

In summary, de Vries behavior emerges quite naturally from our Landau theory. Equally importantly, conventional behavior also genericlly occurs for different Landau parameters. Thus, the model can accommodate all observed behaviors in *all* systems, and, in addition, predicts many new behaviors not yet seen experimentally, like the first order $A-A'$ and $A'-C$ transitions.

We will now briefly describe the formulation and analysis of our theory. A Landau theory for all four phases (I, N, A, C) must include order parameters for three types of order: uniaxial orientational order, layering order and tilt (azimuthal) order. All three are accounted for by the density $\rho = \rho_0 + \delta\rho$ (with ρ_0 constant and $\delta\rho$ spatially varying) and the usual third rank tensor orientational order parameter $\mathcal{Q}$. We take as our Landau free energy[20] $F = F_Q + F_\rho + F_c$, where the orientational[21](F_Q), density (F_ρ), and coupling (F_c) free energies are given by:

$$F_Q \;=\; \int d^3r\left[\frac{t_n Tr(\mathcal{Q}^2)}{12} - \frac{wTr(\mathcal{Q}^3)}{18} + \frac{u_n(Tr(\mathcal{Q}^2))^2}{144} + \;K_n(\partial_i Q_{jk})(\partial_i Q_{jk})\right], \quad (3)$$

$$F_\rho = \int d^3r\left[\frac{t_s'}{4}\delta\rho^2 + \frac{u_s}{24}\delta\rho^4 + \sum_{m=1}^{\infty} C_m\delta\rho\nabla^{2m}\delta\rho\right], \quad (4)$$

$$F_c \;=\; \int d^3r\Big[-\frac{1}{4}Q_{ij}\sum_{m=0}^{\infty} g_{1,m}(\partial_i\rho)(\partial_j\nabla^{2m}\rho) + \;\frac{g_2}{4}Q_{ik}Q_{kj}(\partial_i\rho)(\partial_j\rho) + \frac{g_3}{8}(Q_{ij}(\partial_i\partial_j\rho))^2 + \;\frac{h}{24}(Q_{ij}(\partial_i\rho)(\partial_j\rho))^2\Big], \quad (5)$$

where ∂_i is the spatial derivative in the ith direction, and the Einstein summation convention is implied. The constants u_s, K_n, w, u_n, $g_{1,m}, g_2, g_3$ and h are positive.

We have for simplicity dropped some terms (e.g., $Tr(\mathcal{Q}^2)\delta\rho^2$) that are actually lower order in the presumed small fields $\delta\rho$ and $\mathcal{Q}$ than the terms we have kept. We have verified that keeping such terms with small, but non-zero, coefficients has no qualitative effect on our results. In contrast, dropping any one of the terms we *have* kept is unphysical. For example, dropping the h term destabilizes the C phase[20]. We treat t_n and t_s' as the *only* parameters that depend on temperature.

We seek the configuration of ρ and $\mathcal{Q}$ that minimizes F. The configuration of ρ that does so, is in the smectic phases, spatially modulated along an arbitrary direction which we choose to call z. It can be rewritten in terms of the spatially constant complex translational (or layer) order parameter Ψ, as $\delta\rho = \Psi e^{iqz} + \Psi^* e^{-iqz}$, with layer spacing $d = 2\pi/q$. With ρ of this form, ∂_i can effectively be replaced by $q\delta_{iz}$, which in turn allows us to define $k(q^2) \equiv \sum_{m=1}^{\infty} C_m q^{2m}$ and $g_1(q) \equiv \sum_{m=0}^{\infty} g_{1,m} q^{2m}$. In order for smectic phases to occur, $k(q^2)$ must have a minimum at some value $q_0 \neq 0$ of q. In the absence of the coupling term F_c, and of fluctuations, q_0 is the layering wavevector the system would spontaneously select. Hence, if the coupling terms and fluctuations are small, as we will assume, q will be close to q_0, and we can expand $k(q^2)$ around q_0^2, thereby rewriting Eq.(4) as

$$f_\Psi \;=\; \frac{1}{2}t_s|\Psi|^2 + \frac{1}{4}u_s|\Psi|^4 + \frac{1}{2}K(q^2-q_0^2)^2|\Psi|^2, \quad (6)$$

where we drop oscillating terms, e.g., $\Psi^2 e^{2iqz}$, whose $\int d^3r$ vanish, and define $f_\Psi = F_\rho/V$, where V is the volume, and $t_s \equiv t_s' + k(q_0^2)$ and $K \equiv \frac{\partial^2 k(q^2)}{\partial (q^2)^2}|_{q=q_0}$.

The form of $\mathcal{Q}$ that that minimizes F [19] is spatially uniform, and given by:

$$Q_{ij} = (-S+\sqrt{3}\eta)e_{1i}e_{1j} + (-S-\sqrt{3}\eta)e_{2i}e_{2j} + (2S)e_{3i}e_{3j}\ , \quad (7)$$

where $\hat{\mathbf{e}}_\mathbf{3} = \mathbf{c} + \sqrt{1-c^2}\hat{\mathbf{z}}$ is the average direction of the molecules' long axes, (i.e., the director). Here, in either smectic phase, we chose $\hat{\mathbf{z}}$ normal to the layers; in the N and I phases the direction of $\hat{\mathbf{z}}$ is arbitrary. The projection $\mathbf{c}$ of the director onto the layers is the order parameter for the C phase. The other two principal axes of $\mathcal{Q}$ are given by $\hat{\mathbf{e}}_\mathbf{1} = \hat{\mathbf{z}} \times \hat{\mathbf{c}}$ and $\hat{\mathbf{e}}_\mathbf{2} = \sqrt{1-c^2}\hat{\mathbf{c}} - c\hat{\mathbf{z}}$. S and η are proportional to the birefringence and biaxiality of the system, respectively. The A phase is untilted ($\mathbf{c} = \mathbf{0}$) and uniaxial ($\eta = 0$), while the C phase is tilted ($\mathbf{c} \neq \mathbf{0}$) and biaxial ($\eta \neq 0$). It is convenient to make the change of variables $S = M\cos(\alpha)$ and $\eta = M\sin(\alpha)$. In the A phase, M is proportional to the birefringence.

We next minimize the free energy F over the variables $M, \alpha, c, |\Psi|$ and q. Four qualitatively different types of minima are possible, corresponding to the four different symmetry phases (I, N, A, C). Specifically, the I phase has $M = 0; \Psi = 0$; the N phase has $\Psi = 0$, $\mathbf{c} = \mathbf{0}$, and $\alpha = 0$, but $M \neq 0$; the A phase has $\Psi \neq 0$ and $M \neq 0$, but $\mathbf{c} = \mathbf{0}$, and $\alpha = 0$; and the C phase has all of the variables $M, \alpha, \mathbf{c}$, and $\Psi \neq 0$. We render minimization analytically tractable by assuming that the coupling term Eq. (5) is small, and treating it perturbatively. This procedure leads to the phase diagram shown in Fig. 1.

Equations for the locii of the phase boundaries are given in [22]. The minimization of our Landau free energy also leads to predictions for the temperature dependences of M and q. We find, in the A-phase,

$$M_A \;=\; M_0(t_n) + \frac{q_0^2\Psi_0^2}{\gamma}\left(-3g_2M_0 + \delta\right)\ , \quad (8)$$

$$q_A^2 \;=\; q_0^2 + \frac{M_0}{K}(-g_2M_0 + g_1'(q_0)q_0^2 + \delta)\ , \quad (9)$$

where $\gamma \equiv wM_0 - 2t_n > 0$ and $M_0 = (w + \sqrt{w^2 - 4u_nt_n})/2u_n$ is the "bare" value of M, i.e. its value in the absence of coupling. Likewise, $\Psi_0 = \sqrt{-t_s/u_s}$ is the bare value of Ψ and $g_1'(q_0) \equiv (\frac{dg_1(q)}{dq})|_{q=q_0} \geq 0$. A small value for $g_1'(q_0)$ corresponds to a weak dependence on layer spacing of the coupling between layering and orientational order. For strongly T dependent t_s and athermal t_n the quantity δ is most usefully expressed as

$$\delta(t_s, t_n) \;\equiv\; \alpha(t_s - t_s^{AC})\ , \quad (10)$$

where $\alpha = (2hq_0^2M_0)/u_s$ and $t_s^{AC} = (u_sg_3 - \alpha h(g_1(q_0) - g_2M_0))/h$ is the value of t_s where δ vanishes and the 2nd order AC transition occurs. In the A phase, $\delta > 0$ and in the C phase $\delta < 0$. In the C phase we find

$$M_C \;=\; M_0(t_n) + \frac{q_0^2\Psi_0^2}{\gamma}\left(-3g_2M_0 - \frac{g_2\delta}{2q_0^2(g_3 + h_1\Psi_0^2)}\right), \quad (11)$$

$$q_C^2 \;=\; q_A^2(t_s^{AC}) - \frac{g_1'(q_0)}{2K(g_3 + h\Psi_0^2)}\delta\ , \quad (12)$$

Finally, in the A'-phase, we find:

$$M_A' \;=\; \frac{q_0^2\Psi_0^2g_1(q_0)}{t_n}\ , \quad (13)$$

$$q_A'^2 \;=\; q_0^2\left(1 + \frac{2g_1^2(q_0)\Psi_0^2}{Kt_n}\right)\ . \quad (14)$$

These results imply de Vries behavior for both birefringence and layer spacing. For a nearly horizontal experimental locus like path (ii) through the A phase, the T dependence of M (and hence birefringence) in Eq. (8) comes from the linear t_s-dependence of each of Ψ_0^2 and δ in the correction due to the coupling of layering and orientational orders. From Eq. (8) we see that the de Vries behavior, i.e. non-monatonicity, of M is due to a competition between the layering order, Ψ_0^2 and the coupling δ which increase and decrease respectively as the AC transition is approached. This happens because, as the system moves deeper into the A phase, the layering order increases, thereby augmenting the weak orientational order due to the coupling between the two. However, as the AC transition (where at the director tilts away from

the layer normal) is approached, this coupling necessarily decreases, and, hence, so does M_A. It is straightforward to show that if $g_2 < 2hq_0^2 t_s^{AC}/3u_s$ (i.e. if g_2 is sufficiently small) then this maximum is *inside* the A phase. Thus we expect to see de Vries behavior in systems with weak coupling between layering and orientational order.

As the AC transition is approached within the A phase, q_A monatonically decreases and hence d monatonically increases. This is typical of both conventional *and* de Vries smectics, although as discussed above, it is somewhat contrary to the diffuse cone picture. The T dependence of the layer spacing at the transition depends crucially on the size of the parameter $g_1'(q_0)$. In systems where the coupling of the layering and orientational order depends weakly on layer spacing and g_1' is unusually small, the T-dependence of q is almost flat. We have shown that if $g_1'(q_0) = 0$ then the change in layer spacing scales like $(T_{AC} - T)^3$, and hence varies very weakly in the C phase near the AC transition. Systems with larger values of $g_1'(q_0)$ will have conventional behavior of the layer spacing. Since this de Vries behavior of q depends on the smallness of a *different* parameter (g_1') than did de Vries behavior of M (which depended on g_2 being small), it should be possible to find systems which exhibit de Vries behavior of the layer spacing , but *not* de Vries behavior of the birefringence, or visa-versa.

For systems that approach the C phase from the A' phase, along path (iii), the birefringence will increase monatonically, and will not exhibit de Vries behavior. The birefringence jumps substantially at the transition (on the order of M_0). From Eq. (14), we see that the T dependent piece of q_A' is second order in the coupling $g_1(q_0)$ which we treat perturbatively in our analysis. Thus, this T dependent piece is very small in the A phase. Upon entry into the C phase the T dependence of the layering spacing will be weak if $g_1'(q_0)$ is small. At the $A'C$ transition there will be a jump in q. Eqs. (9), (12) and (14) can be used to show that this jump will be small when $g_1'(q_0)$ and g_2 are small. For such a system a transition just above the CEP will exhibit a continuous change in tilt angle, a weakly varying layer spacing, a substantial jump in birefringence, and a latent heat. Elements of such an unusual transition have been experimentally observed [9].

The requirement of near T-independence of t_n for de Vries behavior severely restricts the possible experimental locii in Fig. 1 that can display such behavior: namely, nearly horizontal ones. A significantly sloped path like (i) will *not* exhibit de Vries behavior. In this case the growth of the "bare" (i.e., coupling-free) birefringence $M_0(t_n)$ as T is lowered swamps the effects due to the coupling terms, and makes the behavior of both the birefringence and the layer spacing conventional. Thus, our model can accomodate *either* conventional behavior or de Vries behavior, simply by changing parameters.

We acknowledge very helpful discussions with Yuri Panarin. K.S., D.H, S.P. were sponsored by the Department of the Navy, Office of Naval Research.

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